A Novel Scheme of Self-Healing Intelligence on Fuel Cladding for Water-Cooling Nuclear Reactors

	だん　しん　ごう
氏　　名	段　　振　　剛
授　与　学　位	博士（工学）
学位授与年月日	平成３０年９月２５日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科(博士課程)量子エネルギー工学専攻
学位論文題目	A Novel Scheme of Self-Healing Intelligence on Fuel Cladding for Water-Cooling Nuclear Reactors (水冷却型原子燃料被覆管における自己修復機能新概念の構築)
指　導　教　員	東北大学教授　笠田　竜太
論文審査委員	主査　東北大学教授　笠田　竜太　東北大学教授　長谷川　晃 東北大学教授　秋山　英二　教授　阿部　弘亨 （東京大学）

論 文 内 容 要 旨

With the world energy crisis and environmental issues intensifies, human being is struggling to reduce the reliance to the fossil fuel as the primary energy source by introducing more of nuclear power, natural power including solar energy, wind power, geothermal energy, and hydro-energy. However, natural power could not be the substitute for the fossil fuel to fulfill the demand of rapid economic growth and modernization due to the restriction from the geographical location and climatic conditions. By contrast, as a low carbon energy source, nuclear power contributes to the stability of the energy supply-demand structure, and the diversification of the energy sources in the world. But everything has two sides. Nuclear safety Nuclear accident, such as Chernobyl nuclear disaster, Fukushima accident, has never been about a country, but it has been about the whole nuclear power industry in the world and even the human survival and development, therefore, safety is the life of the nuclear power. Since Fukushima accident, researchers have been searching for new substitute materials or reliable coating techniques for the fuel cladding to avoid the Zr-steam reaction in loss-of-coolant-accident (LOCA) condition, thereby widening the safety margin of the nuclear. To develop a coating for the current cladding is the main motivation in this research work due that it is possible to put this technique into service in a short-term time with lower investment comparing with the development of new materials.

The preliminary experiments were conducted to check the feasibility of the conventional coatings, namely Al_2O_3 and ZrO_2 coating with the thickness of 100 μm by thermal spraying. The stability and corrosion resistance of these two coatings were assessed by the autoclave and electrochemical experiments, and results revealed that micro-cracks were observed on the as-received coatings, and pores were scattered in the ZrO_2 coating; in the high-temperature aqueous environment, Al_2O_3 was hydrated into AlOOH, which was accompanied by the decrease in the nano-hardness; t-ZrO_2 was transferred into m-ZrO_2, and ZrO_2 coating peeled after the 7-days immersion; the charge transfer resistance (R_{ct}) of the coated samples were much larger than the resistance of the electrolyte into the pores of the coating (R_c), thus, the corrosion resistances of the coated samples mainly depended on the substrate; R_{ct} of the uncoated sample was larger than that of the coated samples, which was consistent with the phenomenon that corrosion current density of uncoated sample was lower than that of the coated samples in the potentiodynamic polarization curves; the as-received cracks and pores, forming

during the fabrication, were confirmed as the common and critical defects for the coatings, and caused the failure to protect the matrix.

It is worth noting that the cracks may be caused during transportation and installation. Therefore, the coating should have the self-healing ability to heal the cracks. The deposition of the chemical-reaction products may be a practical solution to heal the cracks. Based on this consideration, the following works were done to determine the structure of the coating as well as the self-healing reactions.

To avoid the foreign substances into the reactor core, the existing substances in the reactor are selected preferentially as the materials for the coating. The corrosion products in the coolant of light water reactors (LWRs) are mainly made up of the transition-metal compounds, and most of the transition-metal molybdate compounds are water-insoluble. Additionally, MoO_3 is slightly water-soluble, so MoO_3 could react with water to form molybdate ions, or directly react with transition metal ions or oxide compounds to produce molybdate compounds. Thus, it seems possible that the products of the reactions between MoO_3 and the corrosion products could be applied to heal the cracks when depositing, and the possible processes were schematically shown in **Fig.1**.

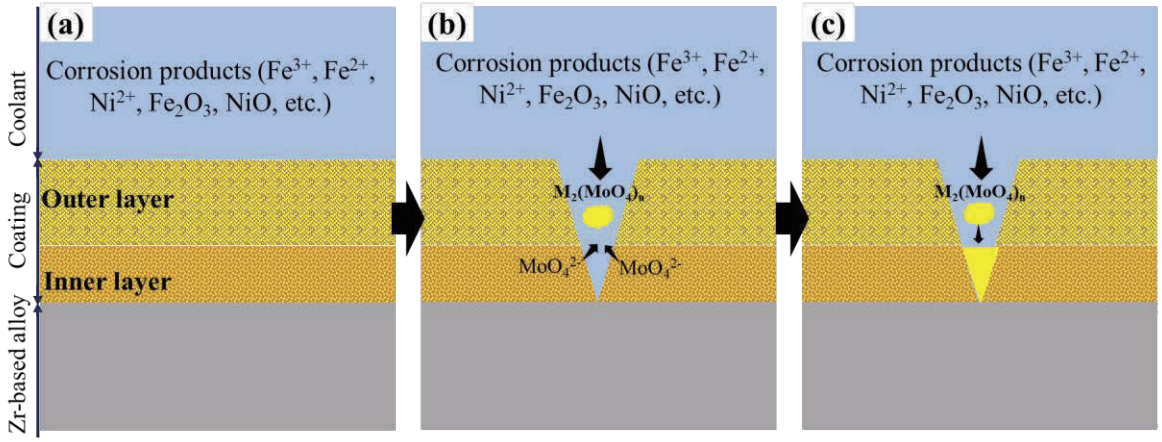

Fig.1 *The schematic graph of the desirable self-healing process. (a) the structure of the coating; (b) crack occurs and molybdate compounds ($M_2(MoO_4)_n$)form; (c) molybdate compounds deposits and crack is filled.("M": transition metal)*

Based on above background, MoO_3 was used as the one of reactants for the self-healing reactions and the main corrosion products, namely Fe_2O_3, Cr_2O_3, ZrO_2, FeOOH, $Cr(OH)_3$, and $Zr(OH)_4$, and two complementary materials: TiO_2 and SiO_2 were chosen as the candidate materials for the other reactants or for the coating. The batch autoclave system and the furnace were employed to simulate the normal condition (360 ℃, saturated pressure, aqueous environment) and abnormal conditions (high-temperature air and steam environment), respectively. The stability and compatibility of the candidate materials with MoO_3 were assessed under normal and abnormal conditions, and the results showed that Fe_2O_3, $Cr(OH)_3$ and $Zr(OH)_4$ reacted with MoO_3 and produced corresponding molybdate compounds while others were compatible with MoO_3 under normal condition. Under abnormal conditions, Fe_2O_3, Cr_2O_3, and ZrO_2 start to react with MoO_3 at 400-650 ℃, producing molybdate compounds; Cr_2O_3 and Fe_2O_3 were stable under normal and abnormal conditions, while ZrO_2, SiO_2, and TiO_2 had phase transformation under abnormal conditions. Additionally, these molybdate compounds would be stable until 800 ℃ according to the literature review.

According to the above findings, this self-healing coating could be designed as the bilayer structure: outer layer and

inner layer. As the passive layer, the outer layer is expected to prevent the inner layer and the matrix under normal condition from contacting with the coolant or other oxidative compounds. As the active layer, the inner layer, consisting of MoO_3, is expected to react with the corrosion products, such as Fe_2O_3, $Cr(OH)_3$, and $Zr(OH)_4$, thus healing the coating by producing the water-insoluble molybdate compounds when the crack occurs. The ZrO_2-Cr_2O_3 composite and ZrO_2-Cr_2O_3-MoO_3 composite can be used as the outer layer and the inner layer, respectively, since the ZrO_2, Cr_2O_3 don't react with MoO_3 under normal condition but could react with MoO_3 under abnormal conditions to enhance the adhesive strength of the coating. The stable phases of TiO_2 and SiO_2 are the suitable as the complement for ZrO_2 and Cr_2O_3.

Since Fe_2O_3 is the main component of the corrosion products and was confirmed to react with MoO_3 under normal condition, Fe_2O_3-MoO_3 reaction showed the potential as the self-healing reaction. Therefore, the Fe_2O_3-MoO_3 reaction was further investigated to clarify the starting temperature and reaction rate. In addition, NiO-MoO_3 reaction could be chosen as the complement for Fe_2O_3-MoO_3 reaction if it would take place under normal condition because NiO is the second largest component of the corrosion products next to Fe_2O_3 in PWR. NiO-MoO_3 reaction was also investigated. As the precursors of the oxides, FeOOH and $Ni(OH)_2$ were chosen as the references in the experiments. In the high-temperature aqueous environment, the starting temperature for FeOOH- and Fe_2O_3-MoO_3 reactions located in 100-200 ℃, and 200-300 ℃, respectively. FeOOH was dehydrated into Fe_2O_3 from the temperature about 300 ℃. As shown in **Fig.2**, for Fe_2O_3- MoO_3 reaction, the molar ratio (C) of $Fe_2(MoO_4)_3$ (reaction product)/Fe_2O_3 as the increase in the immersion time (t) followed the formula:

$$C = 1 - e^{-((3.0\pm1.5)\times t)^{(0.4\pm0.1)}} \quad (1)$$

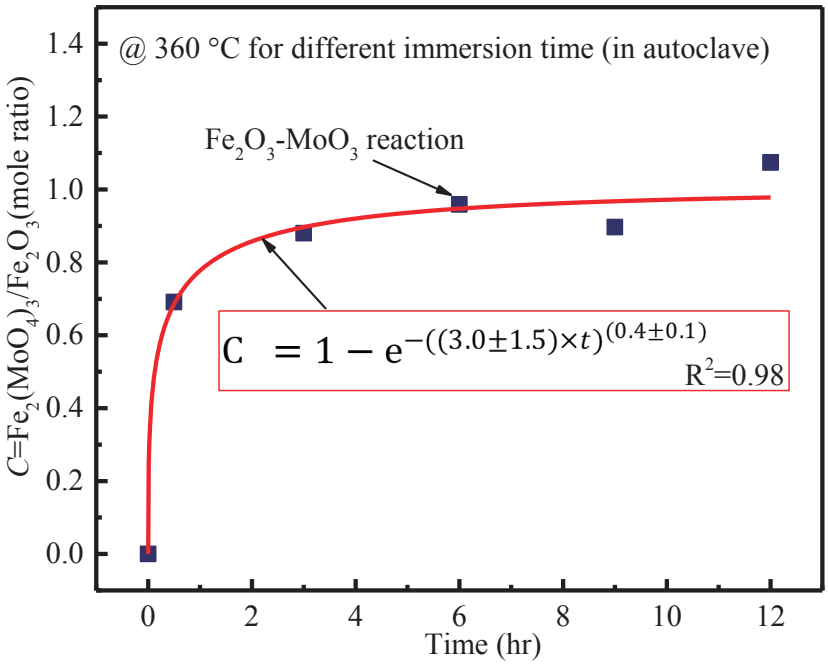

Fig.2 *The molar ratio of $Fe_2(MoO_4)_3/Fe_2O_3$ as the function of the immersion time.*

The rate of Fe_2O_3-MoO_3 reaction approached infinity at the initial time, therefore, the Fe_2O_3 and MoO_3 cannot co-exist together, and react with each other at a fast rate, therefore, the Fe_2O_3-MoO_3 reaction was competent as the self-healing reaction. NiO- and $Ni(OH)_2$-MoO_3 reactions started to proceed almost at the same temperature (around 100 ℃), producing

$NiMoO_4 \cdot nH_2O$ and α-$NiMoO_4$. The $NiMoO_4 \cdot nH_2O$ was favored to form at 200 ℃ while at 360 ℃, its concentration decreased slightly with the increasing immersion time. What's more, the $NiMoO_4 \cdot nH_2O$ had amorphous and crystalline structures and would be dehydrated into β-$NiMoO_4$ at the temperature of about 600 ℃. The rate of NiO-MoO_3 reaction was faster than that of Fe_2O_3-MoO_3 reaction, indicating that it could be utilized as the complementary method for Fe_2O_3-MoO_3 reaction.

As described above, a novel scheme for self-healing intelligence on fuel cladding was proposed through investigation on the physical and chemical stability of the candidate materials, the compatibility of candidate materials with MoO_3, and the potential self-healing reactions, separately. The candidate coating fabrication, other potential self-healing reactions, thermal expansion coefficient, thermal conductivity, and irradiation effects were discussed and analyzed based on the literatures. The sol-gel and thermal spray are the candidate methods for the coating formation. $Zn(CH_3OO)_2$ is injected to the water-cooling nuclear reactors to mitigate the build-up of activated corrosion products, and may react with MoO_3 in the reactor. The reaction product $ZnMoO_4$ may also contribute to the self-healing process. Due to thermal expansion, residual compressive stress along the hoop direction may generate in the coating, and/or gap may form in the substrate/coating interface as well. To avoid the fracture of the outer layer (pure Cr_2O_3 layer), the Cr_2O_3-MoO_3 composite with no more than 25wt.% MoO_3 was recommended for the inner layer. ZrO_2 was not suitable for the coating since the tetragonal and monoclinic phase of ZrO_2 will co-exist during the coating fabrication and the phase transformation from tetragonal to monoclinic phase under normal and abnormal conditions will threaten the stability of the coating. The thickness of the coating should be as thin as reasonably practicable due to its low thermal conductivity. $NiMoO_4$ may be transformed into $CoMoO_4$ since Ni^{58} could be activated to Co^{58} and then decay to Co^{59} in the reactor, however, the irradiation was predicted to make no obvious effects on the spent fuel reprocessing due to the short half-life of Co^{58}. The properties of MoO_3 and Cr_2O_3 under the irradiation have not been investigated to date but irradiation-induced swelling of the coating may take place. In addition, the thermal conductivity of the coating may be deteriorated by the irradiation-induced damages. Meanwhile, the radiation induced surface activation (RISA) effects may enhance the heat transfer on the surface of the coating.

Finally, the technology maturity of the research is estimated by the technology readiness level (TRL). This research started from an idea, and then, the structure of the coating and the candidate materials for the coating and the self-healing process were determined, meaning that the technology maturity of this research has reached the end of TRL3 to date. The future research is to optimize current technologies or develop a new technology for the nuclear application, and then verify the self-healing ability of the coating under normal and abnormal conditions.

論文審査結果の要旨

水冷却型原子燃料被覆管材料のジルコニウム合金の事故耐性を高めるために、様々なコーティング技術の開発が進められている。コーティング材料は、通常運転状態での伝熱効率や原子炉システム全体の安全性を損なうことなく、耐食性を高め、加えて冷却水損失事故シナリオ時のジルコニウム合金の水蒸気反応を防止可能であることが求められる。この中で、セラミックスコーティングは高温での安定性に優れるものの靭性が低いため、き裂の発生の防止もしくは供用中のき裂の自己修復が必要となる。 本研究では、 軽水炉における主要な腐食生成物である遷移金属酸化物が燃料被覆管の（内層）コーティング構成酸化物と反応し安定な生成物を形成することを巧妙に用いて、セラミックスコーティング表面に生じたき裂を自己修復する概念を提案している。

本研究の目的は、上記の自己修復機能を有する新しいコーティング概念の基本となる化学反応系を探索し、その実現可能性を明らかにすることである。

本論文は、これらの研究成果をまとめたものであり、全編７章からなる。

第１章では、本研究の背景と目的について述べている。

第２章では、本研究で実施された実験の方法について述べている。

第３章では、溶射法によってジルコニウム合金表面に形成されたAl2O3もしくはZrO2からなる単一層コーティングの安定性と耐食性について調べ、これらのコーティング中に存在するき裂を治癒するための自己修復反応の必要性を提示している。

第４章では、自己修復反応に資する候補物質を調査し、候補物質の物理的および化学的安定性と、自己修復反応の基本となるMoO3との適合性を高温水環境および大気環境で評価している。これらの評価結果に基づき、自己修復性コーティングの内外層の候補物質を決定し、その結果、Fe2O3-MoO3反応を自己修復反応として用いることができることを示している。

第５章では、自己修復反応への温度と保持時間の影響を明らかにしている

第６章では、第４章および第５章で得られた成果と文献調査に基づいて、自己修復プロセスの実現性、加工性、熱特性、耐照射性の観点から自己修復性コーティングの成立性を多角的に議論し、この議論に基づいて、被覆の製造方法および推奨される化学組成が提案されている。

第７章では、これらをまとめて結論した。

以上のように、本論文は、水冷却型原子燃料被覆管材料に施したセラミックスコーティングのき裂の自己修復機能に適用可能な高温水環境下での化学反応系を実験的に同定し、これらの結果に基づいた自己修復機能の概念を新しく構築しており、量子エネルギー工学の分野に大きく寄与するものと判断される。

よって、本論文は博士(工学)の学位論文として合格と認める。